Partition site occupation embedding theory

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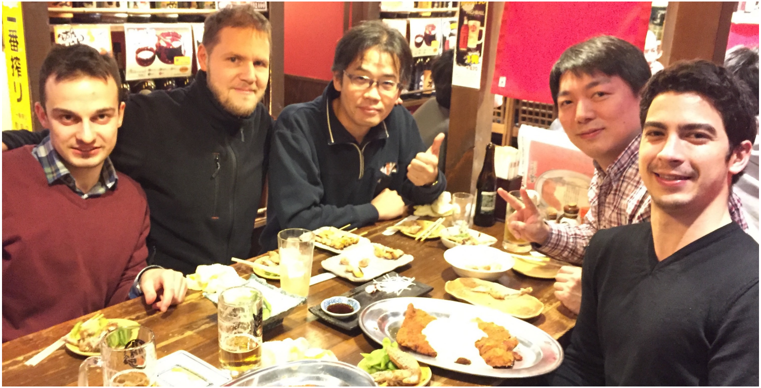
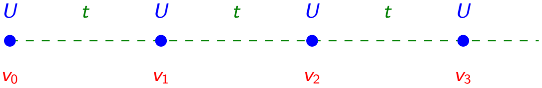
The "SOET team"



From left to right: L. Mazouin, E. F., M. Tsuchiizu (Nara), N. Nakatani (Tokyo), and B. Senjean.

More recently, we started a collaboration with M. Saubanère (Montpellier).

The one-dimensional Hubbard model Hamiltonian



- From a chemical point of view, the Hubbard Hamiltonian is a quantum chemical Hamiltonian written in a basis of *non-overlapping* atomic orbitals where the one- and two-electron *integrals* are *simplified* as follows,

$$h_{ij} \rightarrow -t(\delta_{i,j+1} + \delta_{i,j-1}) + \delta_{ij} v_i \quad \textit{and} \quad \langle ij|kl\rangle \rightarrow U\delta_{ij}\delta_{kl}\delta_{jk}$$

- A *different interpretation* of the model, that is usually adopted by physicists and is convenient for extending density-functional theory (DFT) to model Hamiltonians, relies on the *discretization of* real continuous *space*. The latter is then transformed into a *lattice*.
- In other words, we assume that electrons jump from one point in space (site) to another. The *hopping parameter t* can be interpreted as a *kinetic energy* contribution.
- An electron will also have an energy v_i if it stands on *site i*. This local energy contribution is the analog of the *nuclear potential* (also called external potential) in DFT.
- Finally, two electrons will have a *repulsion energy U* if they occupy the *same site*. Longer-range repulsions are neglected in the model.

DFT for the Hubbard Hamiltonian in a nutshell

- Let us write the Hubbard Hamiltonian as $\hat{H}(\mathbf{v}) = \hat{T} + \hat{U} + \sum_i v_i \, \hat{n}_i$ where $\hat{n}_i$ is the *density operator on site i*.
- Note that $\hat{T}$ and $\hat{U}$ are "universal" in this context (i.e. t and U are *fixed*).
- Let us create the following *ground-state density map* for a fixed *integral number N* of electrons:

$$\mathbf{v} \equiv \{v_i\}_i \quad \rightarrow \quad \Psi_0(\mathbf{v}) \quad \rightarrow \quad \mathbf{n}_0(\mathbf{v}) \equiv \Big\{ \langle \Psi_0(\mathbf{v}) | \hat{n}_i | \Psi_0(\mathbf{v}) \rangle \Big\}_i$$

- According to the *Hohenberg–Kohn theorem*, this map can be inverted (up to a constant):

$$\mathbf{n} \quad \rightarrow \quad \mathbf{v}(\mathbf{n}) \quad \rightarrow \quad \Psi_0\Big(\mathbf{v}(\mathbf{n})\Big) \equiv \Psi_0(\mathbf{n})$$

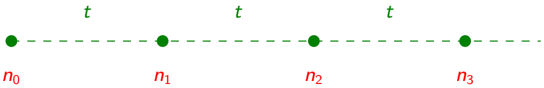
- Moreover, the exact N-electron ground-state energy $E_0(\mathbf{v}, N)$ of $\hat{H}(\mathbf{v})$ can be obtained variationally,

$$\boxed{E_0(\mathbf{v}, N) = \min_{\mathbf{n} \rightarrow N} \left\{ F(\mathbf{n}) + \sum_i v_i n_i \right\}}$$

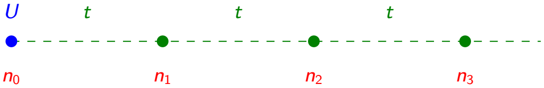
where $F(\mathbf{n}) = \Big\langle \Psi_0(\mathbf{n}) \Big| \hat{T} + \hat{U} \Big| \Psi_0(\mathbf{n}) \Big\rangle$ is the "universal" *Hohenberg–Kohn (HK) functional*.

Kohn–Sham DFT and site-occupation embedding theory

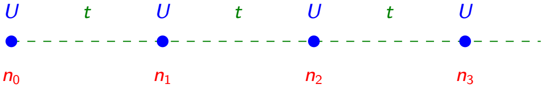
fictitious Kohn–Sham system



fictitious embedded impurity



physical model system



- In *Kohn–Sham* (KS) DFT: $\boxed{F(\mathbf{n}) = T_{\mathrm{s}}(\mathbf{n}) + E_{\mathrm{Hxc}}(\mathbf{n})}$
- In *site occupation embedding theory* (SOET): $\boxed{F(\mathbf{n}) = F^{\mathrm{imp}}(\mathbf{n}) + \overline{E}^{\mathrm{bath}}_{\mathrm{Hxc}}(\mathbf{n})}$

E. Fromager, Mol. Phys. 113, 419 (2015).
B. Senjean, M. Tsuchiizu, V. Robert, and E. Fromager, Mol. Phys. 115, 48 (2017).
B. Senjean, N. Nakatani, M. Tsuchiizu, and E. Fromager, arXiv:1710.03125 (2017).

A flavor of density matrix embedding theory (DMET)

- Let us consider the following expansion of the exact N-electron ground-state wavefunction (in the basis of Slater determinants)

$$\begin{aligned}|\Psi_0(\mathbf{v})\rangle &= \sum_{p_1,p_2,p_3,\ldots\rightarrow N} C_{0,p_1,p_2,p_3,\ldots}|0,p_1,p_2,p_3,\ldots\rangle + \\ &\sum_{p_1,p_2,p_3,\ldots\rightarrow N-1} C_{\uparrow,p_1,p_2,p_3,\ldots}|\uparrow,p_1,p_2,p_3,\ldots\rangle + \\ &\sum_{p_1,p_2,p_3,\ldots\rightarrow N-1} C_{\downarrow,p_1,p_2,p_3,\ldots}|\downarrow,p_1,p_2,p_3,\ldots\rangle + \\ &\sum_{p_1,p_2,p_3,\ldots\rightarrow N-2} C_{\uparrow\downarrow,p_1,p_2,p_3,\ldots}|\uparrow\downarrow,p_1,p_2,p_3,\ldots\rangle \\ &= |0,\Psi^{\rm env.}_{0,N}\rangle + |\uparrow,\Psi^{\rm env.}_{\uparrow,N-1}\rangle + |\downarrow,\Psi^{\rm env.}_{\downarrow,N-1}\rangle + |\uparrow\downarrow,\Psi^{\rm env.}_{\uparrow\downarrow,N-2}\rangle\end{aligned}$$

- If we adpot the point of view of the *impurity site (site 0)*, we need to describe an *open quantum system*.
- One could think of a *single "super" neighbouring site*, referred to as *bath* site, that would play the role of a *reservoir* and integrate informations about the environment.
- Thus we would construct an *embedded impurity* from which (approximate) properties of the system (like the per-site energy) can be extracted. This is the basic idea of DMET*.

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* Knizia and Chan, Phys. Rev. Lett. **109**, 186404 (2012).

Partition DFT applied to the Hubbard Hamiltonian

- A general *density-functional embedding theory* is obtained by partitioning the system into *fragments*.
- The partitioning is *arbitrary*. In quantum chemistry, it is usually driven by the nuclear potentials centered on each atom of the molecule:

$$v(\mathbf{r}) = -\sum_{A}^{\text{nuclei}} \frac{Z_A}{|\mathbf{r}-\mathbf{R}_A|} = \sum_{\alpha}^{\text{fragments}} v^{\alpha}(\mathbf{r})$$

- The density of the full system is then decomposed into *fragment densities:*

$$n(\mathbf{r}) = \sum_{\alpha}^{\text{fragments}} n^{\alpha}(\mathbf{r}).$$

- In practice*, one would first calculate the density of each isolated fragment $n^{\alpha(0)}(\mathbf{r})$ and then reoptimize them in a DFT calculation for the full system.
- The converged fragment densities should reproduce, after summation, the *exact density* of the full system.
- Let us stress that, in partition DFT, the *basic variable* is now the set of fragment densities $\{n^{\alpha}(\mathbf{r})\}_{\alpha}$.

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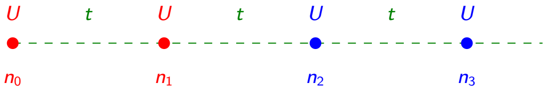
* P. Elliott, K. Burke, M. H. Cohen, and A. Wasserman, Phys. Rev. A. 82, 024501 (2010).

Partition DFT applied to the Hubbard Hamiltonian



- It seems to me (even though I am not completely sure) that partitioning is less ambiguous on a lattice.
- Let us consider the following one,

$$\begin{aligned}\mathbf{n} &= (n_0, n_1, n_2, n_3 \ldots, n_i, \ldots) = (n_0, n_1, 0, 0, \ldots, 0, \ldots) + (0, 0, n_2, n_3, \ldots, n_i, \ldots) \\ &= \mathbf{n}^{emb.} + \mathbf{n}^{env.}\end{aligned}$$

  where the to-be-*embedded* fragment (*emb.*) is separated from the rest of the system, here referred to as the environment (*env.*).

- Note that, in the density-matrix embedding theory (DMET) terminology, *site 0 is the fragment* and the other sites belong to the *environment*.
- in SOET, *site 0 is the impurity* and the other sites are referred to as the *bath*.

Partition DFT applied to the Hubbard Hamiltonian

- Note that, in the particular case of the L-site 1D Hubbard system with uniform density $n = N/L$, the total number of electrons in the embedded fragment is $n_0 + n_1 = 2n = 2N/L$, which gives 0.5 if $N = L/4$.

- Obviously, in this case, we need a DFT for *fractional numbers of electrons*.

- We may actually also consider the following partitioning,

$$\begin{aligned} \mathbf{n} &= (n_0, n_1, n_2, n_3 \ldots, n_i, \ldots) \\ &= (n_0, 2 - n_0, 0, 0, \ldots, 0, \ldots) + (0, n_1 + n_0 - 2, n_2, n_3, \ldots, n_i, \ldots) \end{aligned}$$

  where the embedded fragment is now a *two-electron* Hubbard dimer. In the latter case, *site 1* is playing the role of a *reservoir* that communicates with the rest of the environment.

- What about the following partitioning ?

$$\mathbf{n} = (n_0, n_1, n_2, n_3 \ldots, n_i, \ldots) = (n_0, 0, 0, 0, \ldots, 0, \ldots) + (0, n_1, n_2, n_3, \ldots, n_i, \ldots)$$

- It is unclear how convenient any of these choices would be in practice. They should formally boil down to the same (in-principle-exact) theory.

Interlude on the chemical potential

- Let us consider *non-interacting electrons* ($U = 0$). In the latter case, the many-electron problem boils down to a one-electron problem in which orbital energies must be calculated.

- The many-electron energy is obtained by summing up energies of the *occupied* orbitals.

- Of course, we need to know the number N of electrons. Alternatively, we may *not* specify the value of N and, instead, introduce a shift denoted $-\mu$ into the external potential,

$$\begin{aligned} v_i &\rightarrow v_i - \mu \\ \sum_i v_i \hat{n}_i &\rightarrow \sum_i v_i \hat{n}_i - \mu \sum_i \hat{n}_i = \sum_i v_i \hat{n}_i - \mu \hat{N} \\ \hat{H} = \hat{T} + \sum_i v_i \hat{n}_i &\rightarrow \boxed{\hat{H} - \mu \hat{N} = \hat{H}(\mu)} \end{aligned}$$

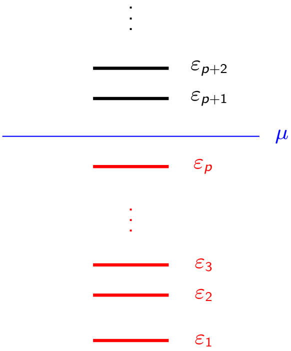
  where $\hat{N} = \sum_i \hat{n}_i$ is the *counting operator*.

- For a given chemical potential μ, we will determine the ground-state energy $\mathcal{G}(\mu)$ of $\hat{H}(\mu)$, which is referred to as the ground-state *grand-canonical energy*.

- Note that the *number of electrons* is *allowed to vary* in the grand-canonical energy minimization.

- As shown in the following, the value of μ will fix the number of electrons.

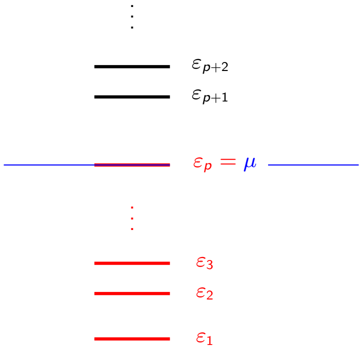
- Most importantly, it will allow us to consider a *non-integral number of electrons* (!).



- Let $\mathcal{G}^N(\mu)$ denote the N-electron grand-canonical ground-state energy.
- In the situation depicted above, we have for $1 \leq k \leq p$

$$\boxed{\mathcal{G}^{2k}(\mu) - \mathcal{G}^{2k-1}(\mu)} = \varepsilon_k - 2k\mu + (2k-1)\mu = \boxed{\mathcal{G}^{2k-1}(\mu) - \mathcal{G}^{2k-2}(\mu) = \varepsilon_k - \mu < 0}$$

- Moreover, if $k \geq p$ then $\mathcal{G}^{2k+1}(\mu) - \mathcal{G}^{2k}(\mu) = \mathcal{G}^{2k+2}(\mu) - \mathcal{G}^{2k+1}(\mu) = \varepsilon_{k+1} - \mu > 0$
- **Conclusion:** $\boxed{\varepsilon_p < \mu < \varepsilon_{p+1} \iff N = 2p}$



- In the situation depicted above, $2p$- and (2p-1)-electron grand-canonical ground-state energies are *equal*:

$$
\begin{aligned}
\mathcal{G}^{2p}(\mu) &= \left(2\sum_{i=1}^{p}\varepsilon_i\right) - 2p\mu \\
&= \left(2\sum_{i=1}^{p}\varepsilon_i\right) - \mu - (2p-1)\mu \\
&= \boxed{\mathcal{G}^{2p-1}(\mu) = \mathcal{G}^{2p}(\mu) \equiv \mathcal{G}(\mu)}
\end{aligned}
$$

- In other words, the $2p$- and (2p-1)-electron eigenfunctions of $\hat{H}(\mu)$ are *degenerate*:

$$\hat{H}(\mu)\left|\Phi^{2p}\right\rangle=\mathcal{G}(\mu)\left|\Phi^{2p}\right\rangle \quad \text{and} \quad \hat{H}(\mu)\left|\Phi^{2p-1}\right\rangle=\mathcal{G}(\mu)\left|\Phi^{2p-1}\right\rangle$$

- *Any* linear combination of these two states is ground state of $\hat{H}(\mu)$:

$$\hat{H}(\mu)\left|\Phi^{\mathcal{N}}\right\rangle=\mathcal{G}(\mu)\left|\Phi^{\mathcal{N}}\right\rangle$$

where $\boxed{\left|\Phi^{\mathcal{N}}\right\rangle=\sqrt{2p-\mathcal{N}}\;\left|\Phi^{2p-1}\right\rangle+\sqrt{\mathcal{N}-(2p-1)}\;\left|\Phi^{2p}\right\rangle}$ with $2p-1\leq\mathcal{N}\leq 2p$.

- Note that $\mathcal{N}$ varies *continuously* from $(2p-1)$ to $2p$ and corresponds to a (possibly fractional) number of electrons:

$$\boxed{\left\langle\Phi^{\mathcal{N}}\middle|\hat{N}\middle|\Phi^{\mathcal{N}}\right\rangle=\mathcal{N}}$$

- The corresponding ground-state density $\mathbf{n}^{\mathcal{N}}$ is a linear combination of $(2p-1)$- and $2p$-electron ground-state densities:

$$n_i^{\mathcal{N}}=\left\langle\Phi^{\mathcal{N}}\middle|\hat{n}_i\middle|\Phi^{\mathcal{N}}\right\rangle=(2p-\mathcal{N})\underbrace{\left\langle\Phi^{2p-1}\middle|\hat{n}_i\middle|\Phi^{2p-1}\right\rangle}_{n_i^{2p-1}}+\Big(\mathcal{N}-(2p-1)\Big)\underbrace{\left\langle\Phi^{2p}\middle|\hat{n}_i\middle|\Phi^{2p}\right\rangle}_{n_i^{2p}}$$

- Note that the *energy varies linearly* with $\mathcal{N}$:

$$\left\langle \Phi^{\mathcal{N}} \middle| \hat{H} \middle| \Phi^{\mathcal{N}} \right\rangle = (2p - \mathcal{N}) \left\langle \Phi^{2p-1} \middle| \hat{H} \middle| \Phi^{2p-1} \right\rangle + \Big(\mathcal{N} - (2p-1)\Big) \left\langle \Phi^{2p} \middle| \hat{H} \middle| \Phi^{2p} \right\rangle .$$

This is the so-called "piecewise linearity of the energy"*

- If we remove the energy contribution from the external potential, we obtain the following *extension of the universal HK functional* to ground-state densities that do *not* integrate to integers:

$$\boxed{F\left(\mathbf{n}^{\mathcal{N}}\right) = (2p - \mathcal{N}) \times F\left(\mathbf{n}^{2p-1}\right) + \Big(\mathcal{N} - (2p-1)\Big) \times F\left(\mathbf{n}^{2p}\right)}$$

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* J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz Jr., Phys. Rev. Lett. 49, 1691 (1982).

DFT for grand canonical ensembles

- Let us consider the full (not necessarily uniform) Hubbard system with a fixed total number of electrons N.
- Alternatively, we may not impose the value of N but, instead, use the corresponding chemical potential μ. The grand-canonical energy is obtained variationally in DFT as follows,

$$\mathcal{G}(\mathbf{v},\mu)=\min_{\mathbf{n}}\left\{F(\mathbf{n})+\sum_i\left(v_i-\mu\right)n_i\right\}$$

- The minimizing density $\mathbf{n}(\mathbf{v},\mu)$ fulfills the following stationarity condition,

$$\boxed{\left.\frac{\partial F(\mathbf{n})}{\partial n_i}\right|_{\mathbf{n}=\mathbf{n}(\mathbf{v},\mu)}=-v_i+\mu}$$

- In a so-called *orbital free* DFT approach, the Kohn-Sham decomposition $F(\mathbf{n})=T_{\rm s}(\mathbf{n})+E_{\rm Hxc}(\mathbf{n})$ would be considered but, rather than solving KS equations, a *density-functional approximation* to $T_{\rm s}(\mathbf{n})$ would be employed and the following equation would hold for any site i:

$$-\left.\frac{\partial T_{\rm s}(\mathbf{n})}{\partial n_i}\right|_{\mathbf{n}=\mathbf{n}(\mathbf{v},\mu)}=v_i+\left.\frac{\partial E_{\rm Hxc}(\mathbf{n})}{\partial n_i}\right|_{\mathbf{n}=\mathbf{n}(\mathbf{v},\mu)}-\mu \qquad \longleftarrow \textbf{KS potential !}$$

Partitioning of the grand canonical energy

- Let us use $\left\{\mathbf{n}^{emb.}, \mathbf{n}^{env.}\right\} \equiv \left\{\mathbf{n}^{\alpha}\right\}_{\alpha}$ as basic variable rather than $\mathbf{n} = \sum_{\alpha} \mathbf{n}^{\alpha}$.

- The grand-canonical energy to be minimized reads*

$$\boxed{F(\mathbf{n}) + \sum_{i} (v_i - \mu) n_i = \sum_{\alpha} \left[F(\mathbf{n}^{\alpha}) + \sum_{i} (v_i^{\alpha} - \mu) n_i^{\alpha} \right] + E_p\left(\left\{\mathbf{v}^{\alpha}, \mathbf{n}^{\alpha}\right\}_{\alpha}\right)}$$

where the partition energy functional equals

$$E_p\left(\left\{\mathbf{v}^{\alpha}, \mathbf{n}^{\alpha}\right\}_{\alpha}\right) = F\left(\sum_{\alpha} \mathbf{n}^{\alpha}\right) - \sum_{\alpha} F(\mathbf{n}^{\alpha}) + \sum_{\alpha} \sum_{i} v_i^{\alpha} \sum_{\beta \neq \alpha} n_i^{\beta}$$

- If the fragment densities do not overlap (which was the case for some partitionings proposed previously) then

$$E_p\left(\left\{\mathbf{v}^{\alpha}, \mathbf{n}^{\alpha}\right\}_{\alpha}\right) \equiv E_p\left(\left\{\mathbf{n}^{\alpha}\right\}_{\alpha}\right) = F\left(\sum_{\alpha} \mathbf{n}^{\alpha}\right) - \sum_{\alpha} F(\mathbf{n}^{\alpha})$$

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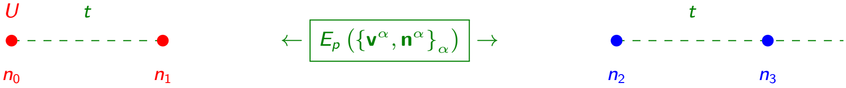
*P. Elliott, K. Burke, M. H. Cohen, and A. Wasserman, Phys. Rev. A. 82, 024501 (2010).

Partition SOET

- In the spirit of **WFT-in-DFT** quantum chemical embedding techniques, we would like to use SOET for the embedded (two-site) fragment and the KS decomposition of $F(\mathbf{n})$ for the environment (like in orbital-free DFT):

$$F(\mathbf{n}^{emb.}) = F^{\rm imp}(\mathbf{n}^{emb.}) + \overline{E}^{\rm bath}_{\rm Hxc}(\mathbf{n}^{emb.}) \quad \text{and} \quad F(\mathbf{n}^{env.}) = T_{\rm s}(\mathbf{n}^{env.}) + E_{\rm Hxc}(\mathbf{n}^{env.})$$



- Stationarity condition for the **embedded fragment**:

$$-\frac{\partial F^{\rm imp}(\mathbf{n}^{emb.})}{\partial n_i^{emb.}} = v_i^{emb.} + \frac{\partial \overline{E}^{\rm bath}_{\rm Hxc}(\mathbf{n}^{emb.})}{\partial n_i^{emb.}} + \frac{\partial E_p\left(\{\mathbf{v}^\alpha,\mathbf{n}^\alpha\}_\alpha\right)}{\partial n_i^{emb.}} - \mu$$

- Stationarity condition for the **environment**:

$$-\frac{\partial T_{\rm s}(\mathbf{n}^{env.})}{\partial n_i^{env.}} = v_i^{env.} + \frac{\partial E_{\rm Hxc}(\mathbf{n}^{env.})}{\partial n_i^{env.}} + \frac{\partial E_p\left(\{\mathbf{v}^\alpha,\mathbf{n}^\alpha\}_\alpha\right)}{\partial n_i^{env.}} - \mu$$